

Synthesis and photoluminescence properties of YPO₄:Eu³⁺ phosphor

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Abstract-

Two different morphological structures of YPO₄:Eu³⁺ have been synthesized by template-assisted routes. A surfactant-mediated synthesis route generated the nanorods, while a complex based precursor solution method to the formation of the nanoparticles. The nanorods have an average diameter of 33 nm and an average length of 290 nm, whereas the spherical nanoparticles show an average diameter of 34 nm. Upon photoluminescence study of the as-prepared samples, the chromaticity of the dopant ion was found to be sensitive to the host morphology as well as the preparative strategy adopted for sample fabrication.

1 Introduction-

Rare earth ion doped compounds have attracted a great amount of interest, due to their significant technological importance, and are used as high-performance luminescent devices, catalysts, time-resolved fluorescence labels for biological detection, and other functional materials based on their optical, electronic, and chemical characteristics.[1-6] The composition and microstructure of the host play an important role in controlling the chemical, physical, optical, and electronic properties of these rare earth ion doped compounds, and also their properties are strongly affected by the synthetic routes [7-9]. Wet-chemistry synthetic routes, such as sol-gel [10,11] precipitation [1,12,13] hydrothermal methods [8,14] etc. are usually employed, as they provide several adjustable parameters such as pH value, reaction temperature, ripening time, and solution concentration and thereby the size, shape, morphology, and structure of the synthesized materials can be effectively controlled. Especially in the synthesis of rare earth doped compounds, the doped ions get uniformly dispersed in the crystal lattice of the host [15, 16] and this gives rise to the enhanced luminescent intensity. However, in the wet-chemistry synthesis of inorganic luminescent materials, luminescent quenchers such as OH-, CO_3^{2-} , etc. can be adsorbed on the material surface and are coordinated with the rare-earth ions. Usually OH ions with high vibrational frequency provide an efficient means to quench the luminescence of rare-earth ions [17]. Phosphors are of enormous importance in scientific and commercial photonic applications, and considerable research in this field is being carried out in the new millennium [19]. Rareearth doped nanocrystals, especially, are being investigated as potential candidates to be used as phosphors in luminescent displays, cold lamps, lasers, amplifiers, upconversion systems, and biological imaging [20-1]. Since the electronic f-f transitions of the rare-earth dopant ions are localized in atomic orbital of the ions, no size dependent quantization effect from confinement of delocalized electrons can be found in these f-ftransitions. However, confinement effect may be induced by inter-ionic electronic interaction, and particularly



through electron–phonon interactions [22], which can visibly influence the optical properties of the phosphors. The spontaneous emission probability of optical transitions from rare-earth ions doped in nanoparticles may, therefore, vary with particle size, shape and nature of the surrounding medium [23-25]. It may also be surmised that the phonon density-of-states of the host material can be significantly modified according to the size and shape of the nanoparticles. Consequently, these changes of non-radiative relaxation probabilities affect the luminescence lifetime, which, in turn, influences the luminescence intensity. Precise control of the size and shape thus allow manipulation of the luminescence properties of the doped nanocrystals [26-30]. It has already been established that as a consequence of the unique electronic structure and the numerous welldefined transition modes involving 4*f* shells of trivalent Eu cations, YPO₄:Eu³⁺ is an important commercial red phosphor, used in color televisions, cathode ray tubes and the high-pressure mercury lamps [31]. YPO₄ crystallizes in a tetragonal xenotime structure, is physically robust and chemically stable, and has drawn much attention from the researchers [32]. In order to mention successful synthetic routes, a detailed understanding of the different crystal structures and nature of the dynamic processes governing the nucleation and growth which ultimately decide the shape of nanocrystals is necessary. Since YPO4:Eu³⁺ is deemed an important lanthanide ion doped nanocrystalline phosphor with potential applications in science and technology. considerable research has been directed at tuning its shape in the nanometer regime.

In the present work, we reported the formation of two morphological structure of $YPO_4:Eu^{3+}$ one-dimensional rod-like structure, and spherical particles. Use of a complex based precursor solution method [50] produced spherical nanoparticles, whereas a surfactant assisted synthesis led to the formation of the nanorods. Subsequently, the impact of different synthetic strategies on the photoluminescence properties of nanocrystalline $YPO_4:Eu^{3+}$ phosphor were systematically studied and compared.

2. Synthesis

2.1. Synthesis of nanorods

A surfactant assisted hydrothermal method was adopted for the synthesis of YPO₄:Eu³⁺ nanorods. 0.09 mol of sodium dodecylsulfate (SDS) was dissolved in distilled water along with continuous stirring. Then, an equimolar mixture of Y(NO₃)₃ and (NH₄)₂PO₄ (2 mmol of each reagent) was dissolved in 40 ml distilled water, along with required amount of Eu(NO₃)₃. In the preparation of 4 different batches of samples, the Eu³⁺ concentration was kept at 1, 3, 5 and 7 at wt% respectively with respect to Y³⁺. The mixture was transferred to a beaker stirred vigorously. The stirring was continued till the mixture became a clear solution. Then, few drop NH₃.H₂O was added to adjust the pH to 9, leading to precipitation. The precipitate was filtered, washed with double distilled water, collected and dried in air. The resultant product was placed in the furnace; the temperature was gradually increased to 800 8C, and the heating was continued for 4 h in order to decompose the surfactant. The product was then cooled to room temperature, and collected for characterization.



2.2. Synthesis of nanoparticles

The nanoparticles of YPO₄: Eu^{3+} were prepared by a complex based precursor solution method, where triethanolamine (TEA) was used as a complexing agent [36]. In a typical synthesis, 2 mmol Y(NO₃)₃, 2 mmol (NH₄)₃PO₄ solution and required amount of Eu(NO₃)₃ solution (as previously mentioned, the Eu³⁺ concentration was kept at 1, 3, 5 and 7 at wt% with respect to Y³⁺ in four different sets) were mixed in a glass beaker, to which 10 ml TEA was added. Then, a few drops of concentrated HNO₃ were added to the solution in order to maintain the pH of the resulting solution at 3–4, thereby avoiding any kind of precipitation. The required amount of TEA was then mixed with the nitrate solution, so that the molar ratio of total metal ion content to TEA was maintained at 1:4. Upon complete dehydration, the nitrates themselves are decomposed with the evolution of brown fumes of nitrogen dioxide, leaving behind a voluminous, organic-based, black, fluffy powder, i.e., the precursor powder. The precursor mass was calcined at 600 °C for 2 h, and then annealed at 800 8C for 4 h to get the required nanoparticles of YPO₄:Eu³⁺.

3. Characterization

3.1 X-ray diffraction method (XRD)

The phase identification was carried out by powder X-ray diffraction at room temperature. Fig. 1 shows the XRD patterns of the as-synthesized phosphors. Both the patterns show the presence of sharp peaks, which could be indexed on the basis of tetragonal xenotime phase of YPO₄ (JCPDS-840335).



Fig. 1. XRD patterns of nanocrystalline YPO₄:Eu³⁺ samples (nanorods and nanoparticles)



4.3.2 Transmission electron microscopy (TEM) and

The morphologies were observed using transmission electron microscopy. The TEM images of nanorods in Fig. 4.2 (a) show the smooth, solid rod-like morphology. Fig. 2(a), the diameter of the nanorods has been estimated to be 33 ± 2 nm. HRTEM image of nanorods, clearly demonstrates the lattice fringes for the tetragonal phase of YPO₄ with a high degree of crystallinity. TEM images of spherical nanoparticles are presented in Fig. 2 (b). The diameter of the spherical nanoparticles to be 34 ± 2 nm.



Fig. 2 TEM image, (a) Nanorods (b) nanoparticle of YPO₄:Eu³⁺ nanoparticles.



Fig. 3 FESEM image, (a) Nanoparticle (b) Nanorods of YPO4:Eu³⁺ nanoparticles.

Fig. 3 (b) shows the field emission scanning electron microscopy (FESEM) images a large number of these pores in the nanoparticles are clearly visible (pointed at by white arrows). A similar image for nanorods reveals the less porous nature of the samples in Fig. 4.3(b). The results obtained from FESEM images were further substantiated with the help of porosity measurements of the samples.



3.3 Photoluminescence

Fig. 4 shows the emission spectra of YPO₄:Eu³⁺ nanorods and nanoparticles. All spectra were taken in an identical condition. In both spectra, a series of resolvable bands appear, peaking at 570–720 nm. These bands are attributed to the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0–2) transitions of Eu³⁺ (4*f*6 configuration) ions, i.e., the band at 586–596 nm is assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, and while the band at 608–620 nm is attributed to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition. The bands in the range of 644–650 and 679–703 nm are due to ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions, respectively [38]. Among the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ transitions of Eu³⁺, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ band at 590 nm is due to a magnetic dipole transition, and hardly changes with the crystal field strength around the Eu³⁺ ion, while the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ band at 617 nm is due to an electric dipole transition of the 4*f* shell, and is highly sensitive to structural changes and environmental effects in the vicinity of the Eu³⁺ ion [40].

From Fig. 4, one can see three striking differences in the emission spectra of nanorods and nanoparticles: (1) the transition intensity ratio $({}^{5}D_{0} \rightarrow {}^{7}F_{2})/({}^{5}D_{0} \rightarrow {}^{7}F_{1})$ of Eu³⁺ is more enhanced in nanorods as compared to spherical nanoparticles, (2) ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ show different splitting patterns in nanorods and nanoparticles, (3) a significant enhancement in the photoluminescence emission intensity of nanorods with respect to nanoparticles is clearly observed from the emission spectra. These three observations may be explained on the basis of known facts.



Fig. 4 Photoluminescence emission spectra of YPO₄:Eu³⁺ nanorods and nanoparticle

3 Conclusions

We report the synthesis of nanocrystalline YPO₄:Eu³⁺ phosphors of two different morphological nanorods and spherical nanoparticles. Surfactant-mediated synthesis was found to be a promising route for the preparation of the nanorods, whereas TEA-assisted complex based precursor solution method led to the formation of the nanoparticles. After routine characterization by XRD and TEM, the photoluminescence properties of the phosphors were studied. The shape anisotropy of the host was reflected in the photoluminescence properties



of the phosphors. The different synthesis approaches also affected the photoluminescence properties of the doped phosphors, by generating different degrees of porosity in the samples.

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